

REPUBLIC OF FRANCE

MINISTRY OF INDUSTRY AND COMMERCE

PATENT OF INVENTION

DEPARTMENT OF INDUSTRIAL PROPERTY

Gr. 14 – Cl. 4 No. 1,070,766

Hair coloring products

Hans Schwarzkopf residing in Germany

Applied for: February 11, 1953, at 2:15 p.m., in Paris

Delivered on February 24, 1954. Published August 12, 1954

(Patent application filed in Germany on February 11, 1952, in the name of the applicant)

Hair coloring products are made almost exclusively from aromatic amines, aminophenols and polyphenols, or their derivatives. These products, called dye bases, are commercially available in appropriate combinations with wetting agents, in liquid form, in combinations with waxes, fats and fat-like products in paste form for paste dyes, or in combinations with synthetic and/or natural gums, in the form of transparent dyes. A coloring agent is formed by the addition of oxidizing agents, especially hydrogen peroxide. The pH of hair dye products can be readily adjusted for a slightly alkaline reaction, and usually ranges from 8 to 10.

When these base dyes are prepared with a finished dye that has a hydrogen peroxide content of about 3%, this results in dyes that color white hair, but do not significantly lighten the color of any remaining natural-colored hair. Therefore, it is difficult to obtain attractive and regular coloring on hair that is somewhat grayed, because

the white hairs are dyed effectively but the natural-colored hairs become darker at the same time. For this reason, in the past if we wished to obtain a uniform coloring job, it was necessary to bleach the natural colored hair first and then to dye the hair afterwards. Attempts have also been made to obtain an equalizing dye of this kind or, as it is called, a "clear dye" by the addition of a larger quantity of hydrogen peroxide. But this result can be obtained only under certain conditions, because when the hydrogen peroxide content is higher, the oxygenation of the dye bases also occurs differently, so that the desired shade is not always obtained.

It has been found that this disadvantage can be eliminated when a sufficient quantity of substances that give rise to carbonic acid, phosphoric acid, and ammonium are added to low-alkalinity hair dyes in quantities of 0.1 to 5% in relation to the base coloring agent.

It has been noted that, in the presence of ammonium ions, both carbonic acid ions and phosphoric acid ions make the hair lighter when it is dyed. However, these effects are different, so the effect produced by the new dyes is very much influenced by the proportion of such ions in the mixture. Phosphorus ions in particular favor a color change toward warm gold tones. For this reason, they cannot be replaced entirely by carbonic acid ions. Ammonium ions are necessary in all cases. The above-mentioned acid ions can also be replaced, in part, by ions of weak acids such as boric acid or by weak organic acids, preferably those which, like tartaric acid, citric acid, ethylene-diamine tetraacetic acid, aminotriacetic acid, and similar acids, can form complex compounds acting as catalysts in the dye formation with the ions of heavy metal salts, particularly iron salts. This is how specific shades can be obtained. When dyes are prepared, the carbonic acid

and phosphoric acid ions probably form percarbonic acid and perphosphoric acid ions that govern the oxidation process that occurs when the hair is lightened and the new hair color is formed, giving rise to the new effects indicated below.

The dyes prepared according to the invention have the property of dyeing hair, even without an increased hydrogen peroxide content, in such a way that the color is evened out and lightened, which was possible in the past only when the hair was bleached in advance. The dyes according to the invention also offer the significant advantage that there is not a great need to take into account how much gray is in the hair, as was necessary in the past. This means that in a single operation, uniform dye jobs can be obtained immediately in the desired shade. For example, unlike what was true in the past, a medium blonde shade colors the hair medium blonde, even if the hair is only 50% gray, whereas without the addition according to the invention, the hair would turn dark blond or light brown. A medium brown applied to hair that is 50% gray, without the addition, yields dark brown, but with the addition according to the invention it results in an attractive and regular light brown.

The practice of adding ammonia to hydrogen peroxide-based hair bleaching products to activate oxygen separation is well-known. In concentrated solutions of hydrogen peroxide, ammonium salts have also been used for this purpose, particularly ammonium carbonate. It has also been long-standing practice to add ammonia or sodium carbonate to hair dyes that are to be developed by hydrogen peroxide to create the necessary alkaline medium. Ammonium ferrous sulfate (for its excellent stability in air) and sodium carbonate (as a saponification product) have been added to hair dye products containing oxidation dyes stabilized by acetyl group to improve shelf life, and these had

to be deacetylated by boiling prior to use in solution. These salts decompose on boiling, so that the finished dye solution no longer contains ammonium ions or carbonic acid ions.

Therefore, all these products are essentially different from the hair dye products that contain the composition according to the invention. Their use does not result in any approximation of the effects or equivalent advantages.

Example 1. Blonde liquid dye.

The following are added to a liquid base product made of water, about 10% soap or soap-like substances and glycerin:

0.5 part toluylenediamine (para)

0.1 part resorcinol

0.3 part picramic acid

1.0 part sodium carbonate

0.5 part ammonium bicarbonate

0.3 part sodium diphosphate

Ammonia is used to adjust the pH to about 10.

For practical use, a mixture is made of about 40 parts dye and 3 parts 33% hydrogen peroxide.

Example 2. Paste dye for dark blonde.

The following are added to 100 parts of a base product in paste form composed of wax-like substances and combined with emulsifiers and water:

1.0 part toluylenediamine (para)

0.5 part resorcinol

1.0 part iron ethylene diamine tetraacetate (iron content about 0.15 part)

0.75 part sodium carbonate

1.0 part sodium diphosphate

Ammonia is used to adjust the pH to about 10. For practical use, a mixture is made with about 40 parts dye and 20 parts 33% hydrogen peroxide.

Example 3. Pomade dye for dark brown.

The following are added to 100 parts of a wax-like base product composed of soaps or soap-like substances in combination with waxes or wax-like substances (softening point about 60°):

15 parts toluylenediamine (para)

0.50 part resorcinol

0.50 part aminophenol (para)

1.5 part ammonium bicarbonate

3 parts sodium carbonate

5 parts potassium hydroxide

30 parts ethanolamine

1.5 part sodium triphosphate

In practice, when it is used for hair coloring, the mass is immersed in 3% hydrogen peroxide and used to coat the hair.

CLAIMS

Liquid, paste, or solid and more or less soapy hair dye product formed from aromatic dye bases, phenols and their derivatives, wetting agents, hydrogen peroxide, alcohols, polyalcohols, fatty products and fat-like substances, characterized in that they

contain substances which, in liquid form, give rise to carbonic acid ions, phosphoric acid ions, and ammonium ions.

In practice, this product may also have one or more of the following characteristics:

- a. The substances that give rise to the ions are added in the form of appropriate carbonates and phosphates, possibly also as ammonia, in a quantity from 0.1 to 5% with respect to the liquid, paste, or waxy base;
- b. Part of the above-mentioned acid ions are replaced by acid ions with low dissociation, such as boric acid, tartaric acid, and citric acid, as well as ethylenediamine tetraacetic acid or aminotriacetic acid;
- c. The product contains additions of acids that form complex compounds with ions of heavy metal salts which can act by catalysis to form the color, particularly metals from the iron group;
- d. The carbonic acid ions are replaced by phosphoric acid ions.

Hans SCHWARZKOPF

Represented by:

Danzen Law Offices